



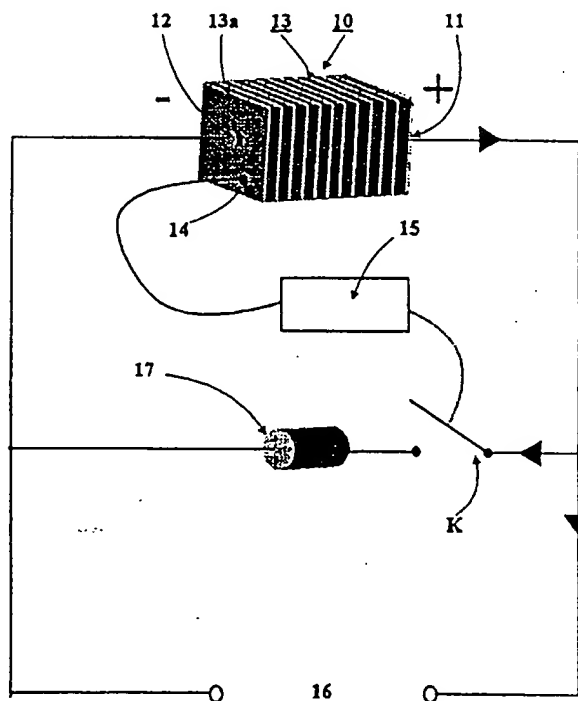
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01M 10/50, 8/04	A1	(11) International Publication Number: WO 95/18469 (43) International Publication Date: 6 July 1995 (06.07.95)
(21) International Application Number: PCT/FI94/00587 (22) International Filing Date: 29 December 1994 (29.12.94) (30) Priority Data: 935936 30 December 1993 (30.12.93) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): SPIERS, David, John [GB/GB]; St. Johns Road, Abingdon, Oxon OX14 2HA (GB). LEPPÄNEN, Jyrki, Rainer [FI/FI]; Yllästunturinkuja 1 D 39, FIN-00970 Helsinki (FI). (74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN- 00100 Helsinki (FI).		(81) Designated States: CA, NO, SE, US. Published <i>With international search report. In English translation (filed in Finnish).</i>

(54) Title: METHOD AND EQUIPEMENT FOR PREVENTION OF COOLING OF ELECTROCHEMICAL DEVICES

(57) Abstract

The invention concerns a method and an equipment for prevention of cooling of electrochemical devices (10). The temperature of the electrochemical device (10) is measured and, as the temperature falls below a certain preset lower limit (T_{minimum}), an additional load (17), which is at least high enough so that the electric current that it produces heats the electrochemical device (10), is connected to the device. The additional load (17) is disconnected from the electrochemical device (10) as the temperature has reached a certain preset upper limit (T_{maximum}).



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Method and equipment for prevention of cooling of electrochemical devices

5

The invention concerns a method for prevention of cooling of electrochemical devices.

10

The invention also concerns an equipment for prevention of cooling of electrochemical devices.

15

Cold climatic conditions cause danger of freezing to electrochemical devices, such as, for example, fuel cells. As is well known, it is possible to use fuel cells connected to a hydrogen storage to produce electric energy in sparsely inhabited regions. Normally, as the fuel cell is in operation, the waste heat which develops in the fuel cells is enough to keep the fuel cell sufficiently warm. However, if the loading is too low to keep the fuel cell sufficiently warm or the fuel cell is not in operation and, thus, is not connected to loading, freezing of the fuel cell can take place. Malfunction in the system may also cause freezing of the fuel cell.

20

25

The most problematic freezing takes place in fuel cells of the solid-polymer electrolyte type. An excessively low temperature may also cause difficulties or at least slowness in the starting in other kinds of fuel cells such as, for example, alkali-type, phosphoric-acid type, etc. In solid-polymer type fuel cells the key component is a membrane which conducts protons, which membrane contains mainly water. If the water in the membrane freezes, it prevents the conducting of the protons in the membrane, and the fuel cell cannot operate. Freezing can also permanently damage the structure of the fuel cell by causing mechanical strain on the cell.

30

Solidification or weakening of the operation at temperatures lower than a normal temperature are also a problem in fuel cells which operate at higher temperatures.

As regards the prior art, reference is made to the publication JP-59-214166, in which publication an outside electric heater is suggested which heats nitrogen gas. By means of this, freezing of phosphoric acid is prevented in phosphoric-acid type fuel cells.

5

The object of the invention is to provide an improvement over the prior-art solutions. A more specific object of the invention is to provide a method and an equipment by means of which it is possible to prevent harmful cooling of electrochemical devices reliably.

10

The method in accordance with the invention is characterized in that the temperature of the electrochemical device is measured and, as the temperature falls below a certain pre-set lower limit, an additional load is connected to the device which additional load is at least high enough to cause an electric current which heats the electrochemical device, and that said additional load is disconnected from the electrochemical device as the temperature has reached a certain pre-chosen upper limit.

The equipment in accordance with the invention is characterized in that the equipment includes a control member, which measures the temperature and carries out the switching-on at a certain low temperature and the switching-off at a certain high temperature, and a member which loads the electrochemical device, which loading member is, by the effect of said control member, switched on at a certain low temperature and causes generation of an electric current which flows through the electrochemical device and heats it, and which loading member is, by the effect of said control member, disconnected at said high temperature to switch off the electric current which heats the electrochemical device.

In the solution in accordance with the invention, the temperature of the electrochemical device, for example the cell battery in a fuel cell, is measured, and as the temperature falls below a certain pre-chosen lower limit T_{minimum} , the additional loading is connected to the electrochemical device. As the additional loading is

connected, the electric current starts to circulate through the circuit which consists of the additional loading and of the inner resistance in the fuel cell. The electric current flowing through the fuel cell then heats the fuel cell, and its temperature starts rising. At the same time, the increased loading automatically produces an increase in the function level of the fuel cell and an increase in the heat generation. The additional loading is disconnected as the temperature of the electrochemical device rises and reaches a certain pre-chosen upper limit T_{maximum} . The waste heat that is formed in the additional load itself can also be used for heating the cell battery by, for example, attaching the additional load concerned near or, for example, even to the cell battery of the fuel cell. It is recommended to measure the temperature from the coldest spot of the set of plates in the fuel cell, for example, from the edge of the set of plates and favourably from the end plate of the cell battery. The temperature can also be measured from inside the cell battery.

The preset lower limit of the temperature T_{minimum} is chosen depending on the kind of electrochemical device that produces electricity that is concerned and on the sort of electrode structure and electrolyte that are used in each case. In all of the cases, the chosen T_{minimum} is higher than the freezing temperature or the solidification temperature of the electrolyte concerned, because freezing or solidification of the electrolyte causes mechanical strains which can be harmful for the fuel cell, and the fuel cell does not start at all when the electrolyte is solid. However, in different types of fuel cells, the normal ranges of operating temperature differ greatly. An electrolyte which contains water is used, for example, in solid-polymer fuel cells (SPFC) and in alkaline fuel cells, in which the range of operating temperature is usually 50...80 °C. Other fuel cell types are solid-oxide type fuel cells (SOFC), whose operating temperature is of an order of 1000 °C, molten-carbonate type fuel cells (MCFC), whose operating temperature is 500...600 °C, and phosphoric-acid type fuel cells (PAFC), whose operating temperature is between 180...300 °C. The operation of the fuel cells deteriorates ever more as the temperature goes down further from the normal operating temperature, and correspondingly it takes longer to reach the normal operation. Thus, according to the invention, it is possible to choose the minimum temperature T_{minimum} in each case at least so high that the fuel

cell still operates at the temperature concerned and it is possible to use the mode of heating in accordance with the invention.

The maximum of the upper limit of temperature T_{maximum} is, naturally, set by the highest permitted operating temperature of the fuel cell type concerned. However, it is advisable to choose the maximum temperature so that it is as close to the minimum temperature as possible in order to minimize the consumption of electricity. A suitable difference in temperature between the upper and lower limits can thus be, for example, 1...20 °C, but it can also be remarkably higher especially in the case of fuel cells that operate at higher temperatures.

It is possible to carry out the connecting and the disconnecting of the additional load in any prior-art way. So it is possible to use a suitable current circuit which consists of one or more temperature detectors and an electric connector member for the purpose.

In its simplest form the additional load can consist of an ohmic resistance, which is connected in parallel with the fuel cell as its temperature falls under the minimum temperature and which is disconnected after the temperature has risen to the set upper temperature value. The resistance value of the resistor is then chosen so that the current flowing through it is not higher than the highest permitted value of the current flowing through the fuel cell.

In accordance with one embodiment of the invention, it is possible to choose the resistance value of the additional load so that it is very low, i.e. the resistance causes a remarkably high load on the fuel cell and thus causes a rapid rise of the temperature. In accordance with the invention, the additional loading can be so high that it causes a current comparable to short circuit of the fuel cell or close to it. In such a case a current circuit is favourably added to the additional load, which circuit cuts the current at a certain frequency and adjusts the width of the pulse by adjusting the effective value of the current to the desired level. By means of pulse-width modulation, it is also possible to adjust the resistance which constitutes an additional load

as an invariable-current load by changing the pulse width. Then the pulse width is proportional to the effective current.

5 The invention will be described in detail with reference to some preferred embodiments of the invention illustrated in the figures in the accompanying drawing, the invention being, however, not supposed to be confined to said embodiments alone.

Figure 1 shows schematically the wiring used in the method in accordance with the invention.

10

Figure 2 shows graphically the supply of the current as a function of time used in the method in accordance with the invention.

15

Figure 3 shows graphically a mode of current supply as a function of time used in a second preferred embodiment of the method in accordance with the invention.

In Fig. 1 the electrochemical device is denoted generally with the reference numeral 10. In this embodiment, the electrochemical device is a fuel cell, whose plus pole is denoted with the reference numeral 11 and the minus pole with the reference numeral 12. The individual cells in the fuel cell are denoted with the reference numeral 13 and the end plate with the reference numeral 13a. The temperature measurement detector 14 is attached to the end plate 13a. The temperature indicator is denoted with the reference numeral 15. The loading of the electrochemical device 10 is denoted with the reference numeral 16.

25

As the temperature indicator 15 shows that the temperature has fallen below the pre-chosen lower limit at the point of time t_0 , the connector K connects the additional load, which is the resistor 17 in this embodiment, to the current circuit, and then the total current is $I_{\text{total}} = I_{\text{loading}} + I_{\text{adjustment}}$.

30

The temperature of the fuel cell 10 rises in accordance with Fig. 2 and, as the temperature reaches the pre-chosen upper limit T_{maximum} at the point of time t_1 , the

connector is disconnected.

In a preferred embodiment of the method in accordance with the invention, it is possible to replace the resistor 17 by invariable-current loading which is controlled
5 by the temperature measurement circuit. The pre-chosen invariable-current loading is chosen so that, with a certain supposed minimum environment temperature $T_{\text{minimum environment}}$, for example -10°C , the temperature of the set of plates in the fuel cell 10 never falls below a certain minimum level, for example $+4^{\circ}\text{C}$. This is a more accurate method and an easier solution than the simple resistance loading
10 system described above, which is illustrated in Fig. 2. It is possible to adjust the invariable-current loading also as a function of the temperature of the environment, which must, however, not be measured too close to the heating resistor or the fuel cell.

15 In a second preferred embodiment of the method in accordance with the invention, it is possible to adjust the invariable-current loading as a function of the change in temperature ΔT in the fuel cell. The change in temperature ΔT is produced by loading. This means that, as the temperature reaches the minimum level T_{minimum} , for example $+4^{\circ}\text{C}$, the invariable-current loading is switched on, for example, to
20 the fuel cell with a certain minimum value. After that, the current I is increased at certain time intervals Δt , if the temperature T of the fuel cell has not increased enough or the temperature T has not increased at all, with a certain invariable amount dI until the upper limit T_{maximum} , for example $+7^{\circ}\text{C}$, has been reached or the speed of the change in temperature T is high enough, as is shown in Fig. 3.

25 Above, only some preferred embodiments of the invention have been described, and it is obvious to a person skilled in the art that it is possible to make numerous modifications to said embodiments within the scope of the inventive idea presented in the accompanying claims.

Claims

1. A method for prevention of cooling of electrochemical devices (10) that produce electricity, **characterized** in that the temperature of the electrochemical device (10)
5 is measured and, as the temperature falls below a certain preset lower limit (T_{minimum}), an additional load (17), which is at least high enough so that the current that it produces heats the electrochemical device (10), is connected to the device, and that said additional load (17) is disconnected from the electrochemical device (10) as the temperature has reached a certain pre-chosen upper limit (T_{maximum}).
10
2. A method as claimed in claim 1, **characterized** in that the electrochemical device (10) is heated by means of additional heat, which is produced by means of a current which flows through the inner resistance in the electrochemical device and which current is caused by an additional load (17) which is connected to the electrochemical device (10).
15
3. A method as claimed in claim 1 or 2, **characterized** in that also the waste heat which is produced by the electric current flowing through the additional load (17) is used for heating of the electrochemical device (10).
20
4. A method as claimed in any of the preceding claims, **characterized** in that said lower limit (T_{minimum}) of the temperature is higher than the freezing temperature or the solidification temperature of the electrolyte in the electrochemical device (10).
- 25 5. A method as claimed in any of the preceding claims, **characterized** in that said upper limit (T_{maximum}) of the temperature is 1...100 °C, preferably 1...20 °C higher than said lower limit (T_{minimum}) of the temperature.
6. A method as claimed in any of the preceding claims, **characterized** in that said
30 additional load (17) is a resistor, a semi-conductor connector transistor, or a combination of same.

7. A method as claimed in claim 6, **characterized** in that the electric resistance of the said additional load (17) is low compared to the inner resistance of the electrochemical device (10).
- 5 8. A method as claimed in claim 6 or 7, **characterized** in that the electric current which flows through said additional load (17) is cut at a certain frequency, and the width of the pulse is adjusted so that the effective current flowing through the additional load (17) is lowered to the desired level.
- 10 9. A method as claimed in claim 1, **characterized** in that an invariable-current load is used as an additional load (17), which invariable-current load is controlled by the temperature (T) measurement circuit.
- 15 10. A method as claimed in claim 9, **characterized** in that said invariable-current loading is chosen to be such that, with a certain supposed minimum environment temperature ($T_{\text{minimum environment}}$) the temperature of the electrochemical device (10) never falls below a certain pre-chosen minimum level.
- 20 11. A method as claimed in any of the claims 1...3, **characterized** in that an invariable-current load is used as said additional load (17), which invariable-current load is adjusted as a function of the outer temperature (T_{outer}).
- 25 12. A method as claimed in any of the claims 1...3, **characterized** in that an invariable-current load is used as said additional load (17), which invariable-current load is adjusted as a function of the change in temperature (ΔT) of the fuel cell or of the environment.
- 30 13. A method as claimed in claim 12, **characterized** in that if the temperature (T) of the electrochemical device (10) has not risen enough or has not risen at all, the current of the invariable-current loading is increased at certain time intervals with a certain invariable amount (dI) until the pre-chosen upper limit (T_{maximum}) has been reached or the speed of the change in temperature (T) is high enough.

14. An equipment for prevention of cooling of electrochemical devices (10) that produce electricity, **characterized** in that the equipment includes a control member (14,15,K), which measures the temperature and carries out the switching-on at a certain low temperature and the switching-off at a certain high temperature, and a
5 member (17) which loads the electrochemical device (10), which loading member is, by the effect of said control member, switched on at a certain low temperature and causes generation of an electric current which flows through the electrochemical device (10) and heats it, and which loading member is, by the effect of said control member, disconnected at said high temperature to switch off the electric current
10 which heats the electrochemical device (10).

15. An equipment as claimed in claim 14, **characterized** in that said loading member (17) is an electric resistor, a semiconductor connector, or a combination of same.

15

16. An equipment as claimed in claim 14 or 15, **characterized** in that said loading member (17) is attached to the end plate (13a) of the electrochemical device (10).

17. An equipment as claimed in claim 14 or 15, **characterized** in that said loading
20 member (17) is attached inside the electrochemical device (10) to an electrically conductive plate that interconnects the cells, said attachment being electrically insulating.

18. An equipment as claimed in any of the claims 14...17, **characterized** in that said
25 electrochemical device (10) is a fuel cell.

1/2

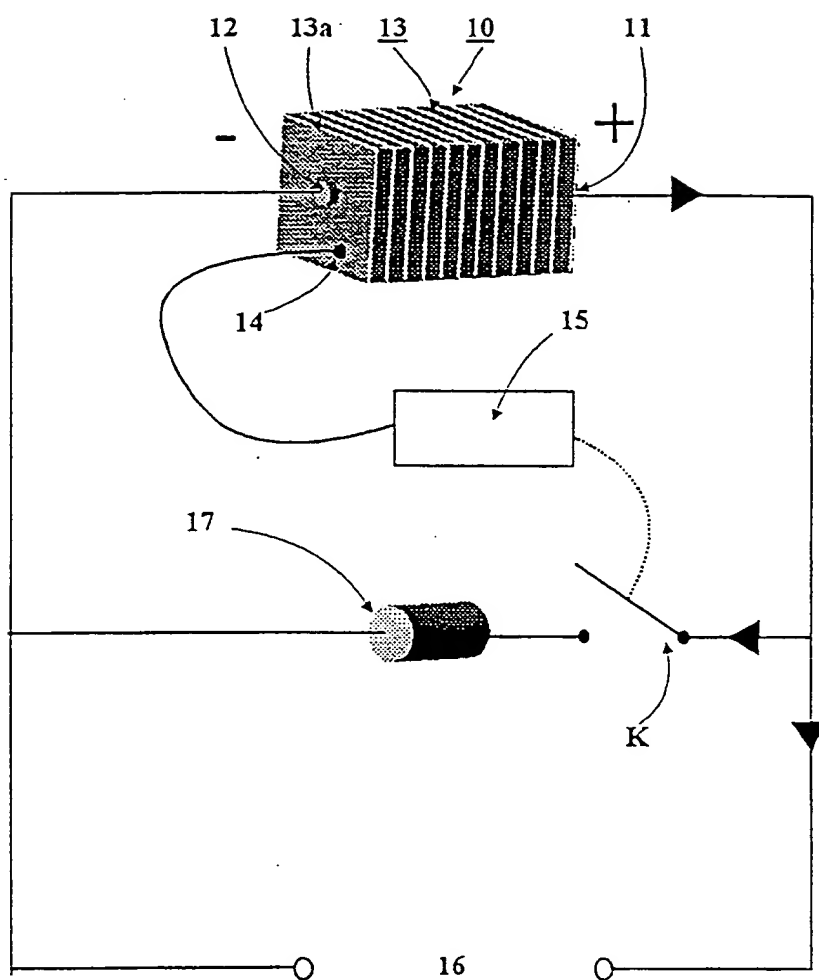


FIG. 1

2/2

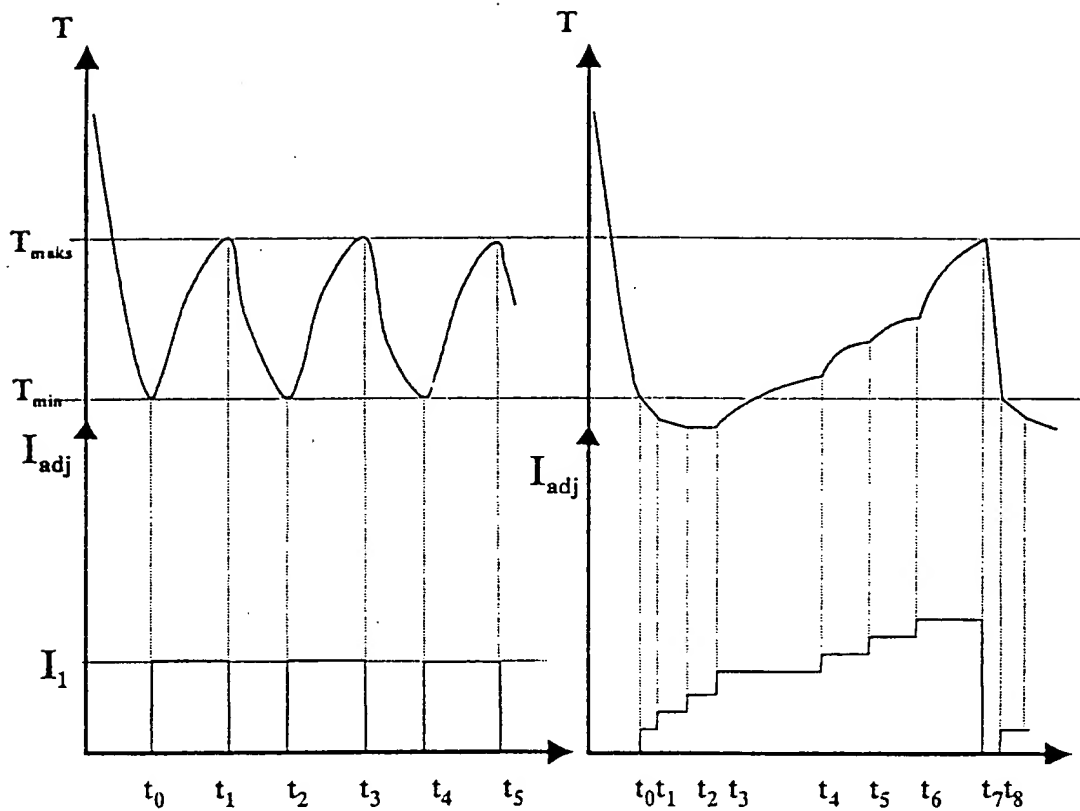


FIG. 2

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00587

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 10/50, H01M 8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, A1, 2643903 (KOLEFF, BORIS), 30 March 1978 (30.03.78)	1,2,14
Y	--	18
X	Patent Abstracts of Japan, Vol 12, No 328, E-654, abstract of JP, A, 63-91967 (HITACHI LTD), 22 April 1988 (22.04.88)	1,14,18
Y	DE, A1, 1496128 (ROOSEN, R.), 12 June 1969 (12.06.69), claims 3,4	18

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 April 1995

Date of mailing of the international search report

13 04 1995

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Ulla Granlund
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00587

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE, A1, 2148627 (VARTA AG), 5 April 1973 (05.04.73), page 1, line 4 - line 11 --	18
A	US, A, 3512071 (H.L. DANIELS), 12 May 1970 (12.05.70), column 1, line 60 - line 65 --	1,14
A	DE, A1, 1496346 (VARTA AG), 14 May 1969 (14.05.69), page 4, line 17 - page 5, line 4 --	18
A	Patent Abstracts of Japan, Vol 9, No 81, E-307, abstract of JP, A, 59-214166 (TOSHIBA K.K.), 4 December 1984 (04.12.84) --	18
A	Patent Abstracts of Japan, Vol 10, No 16, E-375, abstract of JP, A, 60-177568 (MITSUBISHI DENKI K.K.), 11 Sept 1985 (11.09.85) -- -----	18

INTERNATIONAL SEARCH REPORT

Information on patent family members

25/02/95

International application No.

PCT/FI 94/00587

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 2643903	30/03/78	NONE	
DE-A1- 1496128	12/06/69	NONE	
DE-A1- 2148627	05/04/73	NONE	
US-A- 3512071	12/05/70	NONE	
DE-A1- 1496346	14/05/69	NONE	